Energy efficient UV/H_2O_2 processes for conversion of pharmaceuticals in drinking water: effect of water quality

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Abstract

Previous research showed that surface water in the Netherlands may contain significant concentrations of organic micropollutants like pharmaceuticals. A model has been developed which can predict the conversion of a broad range of organic micropollutants in a UV/H_2O_2 process with low pressure UV lamps. This model also was applied to optimize UV reactors, which were tested at three Dutch locations, including two drinking water companies. It was observed that the model predictions were very accurate, that very high conversion could be obtained, and that the optimized UV reactors resulted in a 30-40% reduced energy demand of the process. Furthermore it was shown that the effect of pretreatment of the water, reducing the DOC content and increasing UV-T values, can improve reactor performance by 30-70%.

1 Introduction

The numbers and concentrations of pharmaceuticals in drinking water sources are increasing continuously. In Limburg, the most southern province of the Netherlands, it was found that concentrations of pharmaceuticals and metabolites in surface waters ranges from 7 to 27 μg/L, and wastewater treatment plants in many cases have not been developed to deal with such compounds (Ter Laak et al., 2014; Hofman et al., 2013). Therefore, it is becoming more and more important for drinking water companies to add treatment steps which can remove or convert these compounds, in order to prevent them from appearing in the drinking water. Advanced oxidation processes, like UV/H_2O_2 processes, may be very effective to convert a broad range of different compounds (Mariani et al., 2010).

A kinetic model has been developed, which predicts the conversion of a broad set of pharmaceuticals by means of oxidation and photolysis as a function of the UV dose applied. The model takes into account water quality parameters, like the presence of HCO_3^-, NO_3^-, and NOM, and the temperature. This model was combined with a hydrodynamic flow and UV light distribution model of the UV reactor vessel (Wols et al. 2015). In this way the conversion of the pharmaceuticals could be predicted with a high accuracy. The model can be applied to optimize process parameters, but by calculating the effect of adjustments in the reactor geometry and design, it also appeared possible to design a UV/H_2O_2 reactor which requires 30-40% less energy. This reactor was demonstrated at two different drinking water companies: Dunea and WML. The effect of pretreatment, and thus of water quality, on the process effectiveness was studied.

2 Experimental Information

Some experiments were carried out at Van Remmen UV Technology, using drinking water from the town of Wijhe. At Dunea and WML pretreated surface water was used for testing. Both water companies use water from the river Meuse. At Dunea (site Bergambacht) this is pretreated by means of coagulation, sedimentation, micro sieves and sand filtration, whereas at WML (site Heel) the water was pretreated by means of lake storage (where it is mixed with ground water), bank filtration, aeration and rapid sand filtration. The Dunea water appeared to have a UV transmission of about 75%, and the WML water showed a UV-T of about 94%. In order to study the effect of pretreatment on the water quality and the UV/H_2O_2 process performance, at Dunea an additional pretreatment by means of granular activated carbon or

O_3/H_2O_2 was carried out. Three different types of UV reactors were used, all three built by van Remmen UV Technology: a conventional disinfection reactor (D130), an optimized version of this reactor (D200) and the NEW reactor, which had specially been developed for water with a high UV-T value. This reactor was equipped with four 300 W LP UV lamps and could treat a water flow of 10 m^3/hour. Unfortunately this flow was too high to use this reactor at the pilot facilities at WML. D200 was equipped with one 120 W low pressure UV lamp and two flow plates. A flow between 1 and 2.5 m^3/hour could be applied. At WML only the “D200” reactor was used, whereas at Dunea both D200 and NEW were used. The H_2O_2 concentration was varied at both locations.

In order to remove the excess of H_2O_2 and possibly found transformation products, activated carbon filtration was applied after the UV/H_2O_2 reactor at WML and in Wijhe. At Dunea multiple circulation over the UV reactor was applied for this purpose.

The following pharmaceuticals and organic micropollutants (OMPs) were studied.

Table 1: Pharmaceuticals and OMPs studied

Group (Use)	compounds
Analgesic	AMPH, diclofenac, ketoprofen, naproxen, paracetamol, phenazon, tramadol
Antibiotics	Ciprofloxacin, clindamycin, erythromycin A, Lincomycin, Metronidazole, Sulfachloropyridazine, sulfadiazine, sulfamethoxazole, sulfaquinoxalin, trimethoprim
Cardiovascular	Atenolol, metoprolol, pentoxifylline, pindolol, propranolol, sotalol, bisoprolol
Diuretic	Furosemide
Lipid regulator	Bezafibrate, clofibric acid, gemfibrozil

Antiepileptic	Carbamazepine
Antidepressant	Fluoxetine, paroxetine, venlafaxine
Bronchodilator	Clenbuterol, salbutamol, terbutaline
Glucocorticoid	Cortisol, cortisone, prednisolone
Anticarcinogen	Cyclophosphamide, ifosfamide
antidiabetic	Metformin, uranylgurea (metabolite of metformin)
X-ray contrast	Diatrizoic acid
Psychoactive	Caffeine
Vitamin	Niacin
other	Atrazine, pCBA

These compounds were added in concentrations of mostly 1 μg/L; only Cortisol, Cortisone and Erythromycine A were added at 3 μg/L, Metformin, guanylurea, caffeine and prednisolone were added at 5 μg/L, and pCBA was added at 10 μg/L.

3 Results and discussion

It had been found that the model could predict the conversion of various compounds very well, as was shown in (Wols et al., 2015). Furthermore, experiments at Wijhe showed that in general for all compounds the predicted energy savings of 30-40% could be reached, when D200 and NEW were compared with D130 (Wols et al., 2015b).

3.1 Degradation of compounds at Dunea

It was observed that the conversion of pharmaceuticals at the Dunea site was very high, as is shown in figure 1.

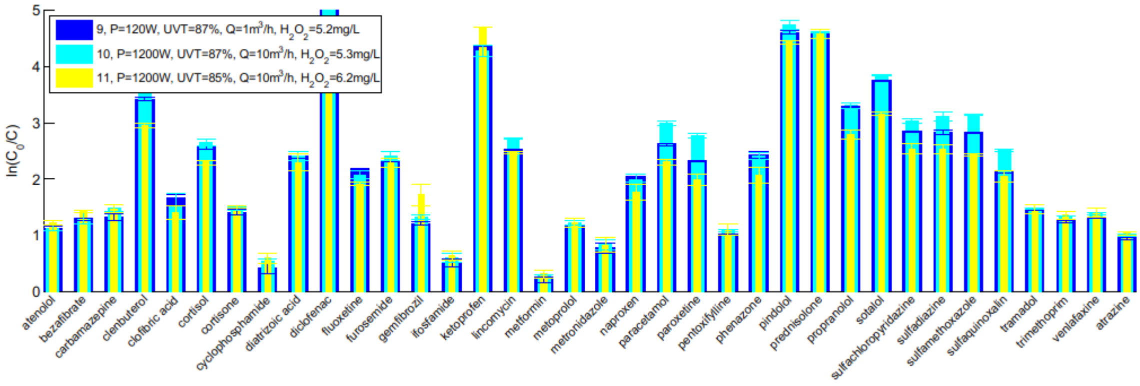

Figure 1: Conversion of pharmaceuticals at the Dunea site

3.2 Degradation of compounds at WML

The UV-T value of pretreated water at WML is about 94%. At first it seemed that the predicted conversions were significantly lower than the actual conversions. This was caused by the fact that reflection of UV irradiation at the reactor wall now had to be taken into account (at Wijhe and Dunea the UV-T was so low, that this factor could be neglected). Introducing reflection of UV radiation at the outer wall into the model gave better results, although the predictions still were a little low. Calculations taking into account UV-T values of 95 and 96% showed that the improvement of UV-T from 94% to 96% during the reaction results in a continuously improving process throughout the reactor, which probably explains the small discrepancy observed. Figure 2 shows both the actual and predicted conversions at a dose of 9.4 mg H_2O_2/L and of 2.8 mg H_2O_2/L. In both cases there still is a fairly good accordance between the predicted and measured values. However, it is shown that decreasing the H_2O_2 concentration results in a less efficient conversion of organic micropollutants.

N.B. For tramadol and terbutalin no kinetic data are available in literature, so for these compounds conversion data could not be predicted.

3.3 Effect of water matrix

At the Dunea site UV-T was about 75%, which is rather low for a UV/H_2O_2 process. By means of pretreatment it was tried to improve the water quality of the influent. It was shown that pretreatment with ozone/peroxide or activated carbon filtration resulted in an improvement in log degradation on the average of about 30-70%. The ACF seemed to be more efficient, as it both increased UV-T and reduced DOC content. The effect of a higher UV-T especially could be observed for the NEW reactor, as this had been designed for a situation with a high UV-T value. The effect of different water matrix compositions on the reactor performance is shown in figure 3.

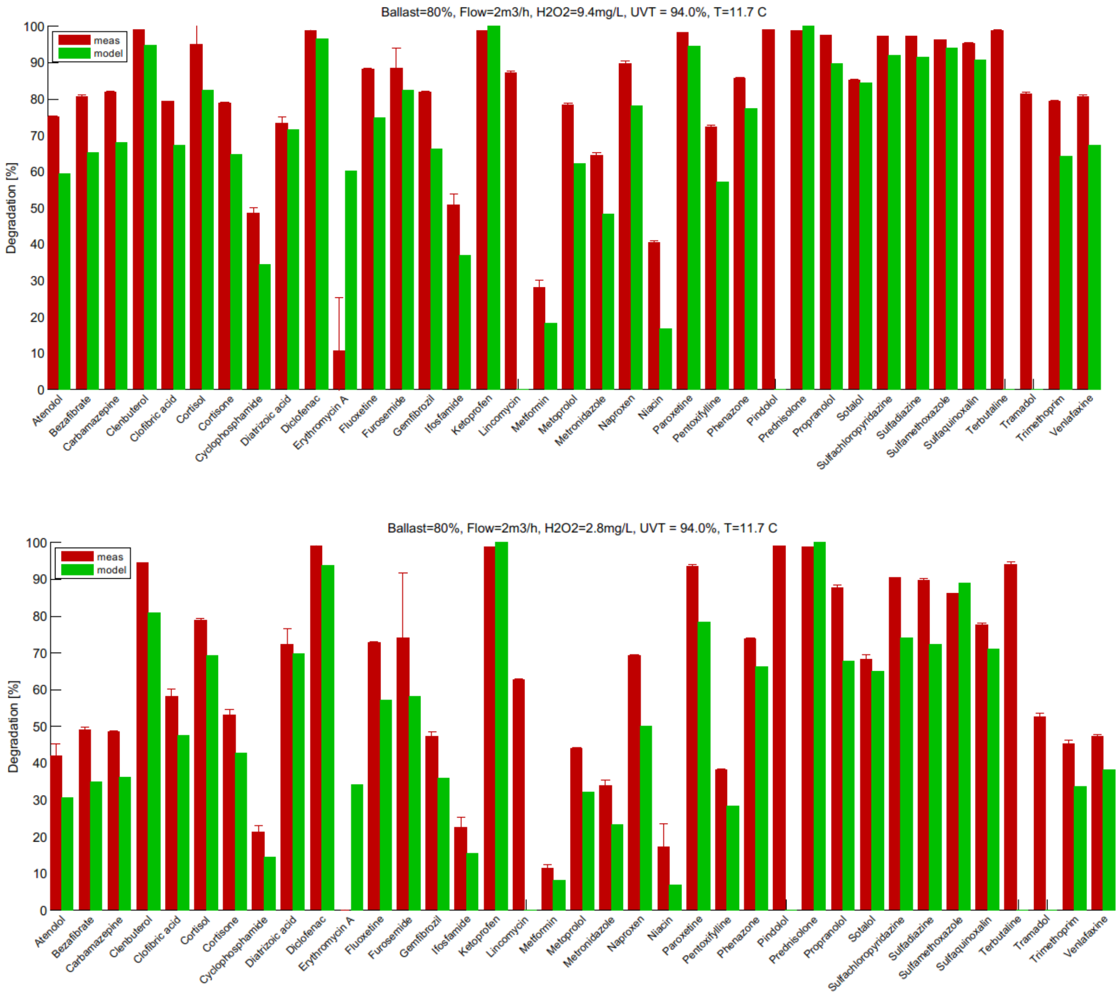

Figure 2: Measured versus predicted conversions at site WML. Upper panel H_2O_2 concentration 9.4 mg/L, lower panel 2.8 mg/L

The E_{EO} for site Heel (blue bars) is very low, due to the very high UV-T of this water. At Dunea, with the lowest UV-T of 81.5%, the E_{EO} values in general are the highest. Obviously, applying O_3/H_2O_2 as a pretreatment

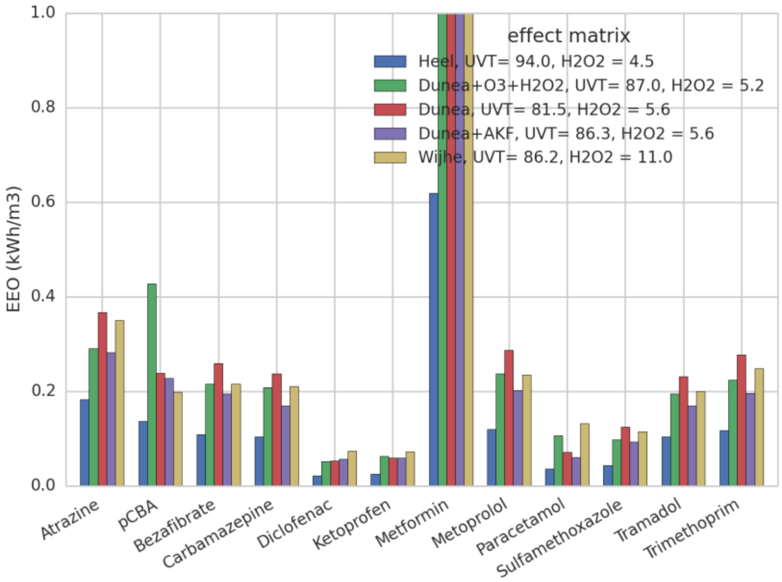

Figure 3: Effect of water matrix composition on reactor performance

(green bars) reduces the E_{EO} values, and an even better reduction can be obtained when ACF is applied (purple bars). At site Wijhe the UV-T is comparable to Dunea with O_3/H_2O_2 pretreatment, which results in a similar E_{EO} value. At the moment we do not have an explanation why pCBA in case of O_3/H_2O_2 pretreatment gives a higher E_{EO} value.

4 Conclusions

- The models developed for UV/H_2O_2 processes give a very reliable prediction of the conversion that can be obtained for several pharmaceuticals and organic micropollutants.

- Reactor D200, which had been optimized using these models, indeed gave at least 30% better conversion at same energy use (or about 30% energy savings, reaching similar conversions).

- Reactor NEW, specially designed for UV-T values >85%, can result in an additional 10% energy savings, but this may also depend on the specific compounds involved.

- At the Dunea site it also was observed that the D200 and NEW reactors gave very good conversion of organic micropollutants. Pretreatment of the water by means of ACF or O_3/H_2O_2, reducing DOC content and increasing UV-T, resulted in a 30-70% better performance of the process.

- At the WML site the UV-T values were so high that reflection of UV irradiation at the reactor wall had to be taken into account. Besides, results even became better because UV-T during the process is increased. As a result of these effects the UV/H_2O_2 process became even more efficient to convert organic micropollutants at very low energy demands.

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6 Literature

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